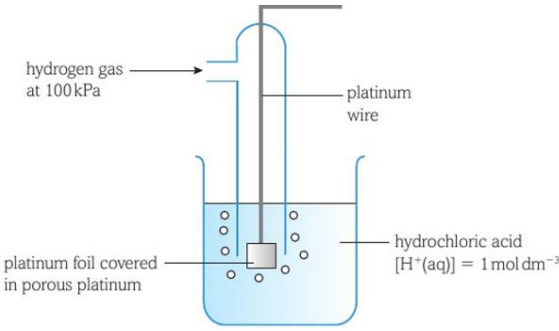


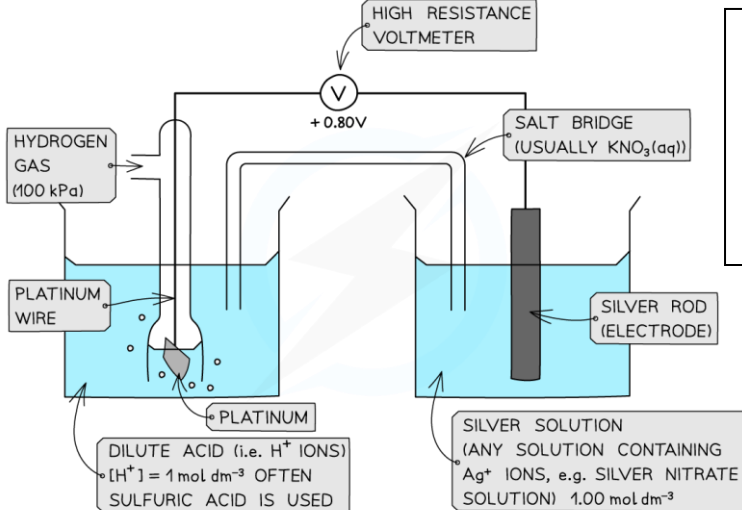
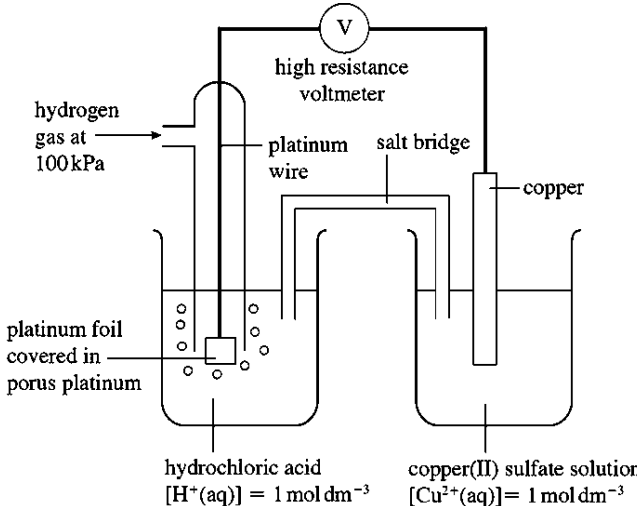
Unit 5: Transition Metals and Organic Nitrogen Chemistry

Topic 16: Redox Equilibria

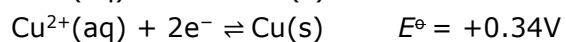
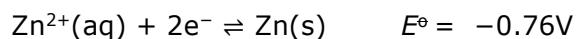
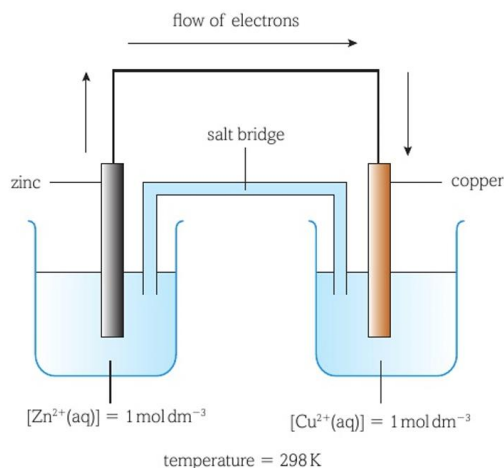
Students will be assessed on their ability to:

These definitions apply to all s-, p- and d-block elements	16.1	understand the terms 'oxidation' and 'reduction' in terms of electron transfer and changes in oxidation number, applied to s-, p- and d-block elements
		<p><u>In terms of electron transfer,</u> Oxidation is the loss of electrons and Reduction is the gain of electrons</p> <p><u>In terms of changes in oxidation number,</u> Oxidation is when the oxidation number of an element in a species increases Reduction is when the oxidation number of an element in a species decreases</p> <p>S-block elements and p-block metals are usually oxidized by losing electrons to form 1+ and 2+ ions P-block non-metals are usually reduced by gaining electrons to form negative ions D-block elements can form various ions due to their variable oxidation state</p>
	16.2	know what is meant by the term 'standard electrode potential', E^\ominus
		<p>Standard electrode potential, E^\ominus = Standard redox potential = "The potential difference (voltage) (electromotive force) measured (using a high resistance voltmeter) when a standard half-cell is connected to a standard hydrogen electrode under standard conditions"</p>
	16.3	<p>know that the standard electrode potential, E^\ominus, is measured in conditions of:</p> <ul style="list-style-type: none"> i 298 K temperature ii 100 kPa pressure of gases iii 1.00 mol dm⁻³ concentration of ions
		<p>Standard conditions for all equilibria are 298K, 100kPa (1 bar) and 1 mol/dm³ concentration of ions in solution</p> <p>This is important as altering the conditions results in changes in position of equilibrium</p> <p>Standard measurements are made using a high resistance voltmeter so that no current flows and maximum potential difference is achieved</p>
	16.4	know the features of the standard hydrogen electrode and understand why a reference electrode is necessary
		<p>STANDARD HYDROGEN ELECTRODE (SHE)</p> <p>Standard hydrogen electrode consists of an equilibrium of H₂ gas at a pressure of 100kPa (1 bar) bubbling over a piece of platinum foil dipped into a solution of HCl(aq) with H⁺ ion concentration of 1 mol/dm³ at a temperature of 298K</p> <div style="display: flex; align-items: center;">  <div style="margin-left: 20px;"> <p>The surface of the platinum foil is covered in porous platinum which has a large surface area that allows an equilibrium to be formed quickly:</p> $\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g}) \quad E^\ominus = 0.00\text{V}$ <p>By convention, the standard electrode potential of the standard hydrogen electrode is 0</p> </div> </div> <p>A reference electrode is necessary to measure the electrode potentials of chemical systems because it is not possible to measure the potential difference (of a half-cell) between the metal electrode and the ion solution</p>

16.5	<p>understand that different methods are used to measure standard electrode potentials of:</p> <ul style="list-style-type: none"> i metals or non-metals in contact with their ions in aqueous solution ii ions of the same element with different oxidation numbers
	<p>There are three different types of half-cells that can be connected with SHE</p> <ol style="list-style-type: none"> 1. Metal Metal ion 2. Non-metal Non-metal ion 3. Ion Ion (of same element but in different oxidation states)
i	<p>Metal metal ion</p> <ul style="list-style-type: none"> - Connect the standard hydrogen electrode (SHE) to the metal electrode via a circuit containing a high resistance voltmeter - The two components are half-cells - A salt bridge completes the circuit (usually the salt bridge is a concentrated solution of KNO_3 or any ionic salt but the salt should not interfere with the half-cells- i.e. no precipitates should form) - A high resistance voltmeter is used so that no current flows and maximum potential difference is achieved to measure the difference in potential between the two half-cells when <i>both reactions are in equilibrium</i> <p><i>The sign of the standard electrode potential indicates the polarity of the electrode when compared with the hydrogen electrode</i></p> <p>Let's consider Ag as the metal:</p> $\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g}) \quad E^\circ = 0.00\text{V} \text{ (negative electrode) (oxidation)}$ $\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) \quad E^\circ = +0.80\text{V} \text{ (positive electrode) (reduction)}$ $E^\circ_{\text{cell}} = 0.80 - 0.00 = +0.80\text{V}$ <p>With Ag, E° is positive which means electrons would flow from the hydrogen electrode to the Ag electrode if the voltmeter was taken out of the circuit</p> <p>This means relative to the hydrogen half-cell, it is more likely to get reduced as it has a more positive E° value</p> <p>A positive E° value means that the equilibrium of the half-cell reaction lies further to the left than the equilibrium of the standard hydrogen electrode</p> <p>Non-metal non-metal ion</p> <p>Let's consider Br_2 as the non-metal:</p> $\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g}) \quad E^\circ = 0.00\text{V} \text{ (negative electrode) (oxidation)}$ $\frac{1}{2}\text{Br}_2(\text{l}) + \text{e}^- \rightleftharpoons \text{Br}^-(\text{s}) \quad E^\circ = +1.09\text{V} \text{ (positive electrode) (reduction)}$ $E^\circ_{\text{cell}} = 1.09 - 0.00 = +1.09\text{V}$ <p>With Br_2, E° is positive which means electrons would flow from the hydrogen electrode to the Br_2 electrode if the voltmeter was taken out of the circuit</p> <p>This means relative to the hydrogen half-cell, it is more likely to get reduced as it has a more positive E° value</p> <p>A positive E° value means that the equilibrium of the half-cell reaction lies further to the right than the equilibrium of the standard hydrogen electrode</p> <div style="border: 1px solid black; padding: 5px; margin-top: 10px;"> <p>Systems involving gases!</p> <p>So how do we actually measure when gases are involved like Br_2 as shown above?</p> <p>Well we do it just like with SHE involving H_2 gas where the gas is bubbled into a solution containing its ions</p> <p>To set up the redox equilibrium, a platinum wire (foil) is placed into solution to act as an electrode to provide an electrical connection between the gas and the ions!</p> </div>

ii	<p>Ion Ion (of the same element with different oxidation numbers)</p>  <p>A platinum electrode is used to form a half-cell of ions that are in different oxidation states Remember that: Reduction occurs at positive electrode Oxidation occurs at negative electrode</p> $\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g}) \quad E^\ominus = 0.00\text{V} \text{ (negative electrode) (oxidation)}$ $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \quad E^\ominus = +1.52\text{V} \text{ (reduction)}$ $E^\ominus_{\text{cell}} = 1.52 - 0.00 = +1.52\text{V}$
16.6	<p>CORE PRACTICAL 12 Investigating some electrochemical cells.</p>
	<p>Draw a suitable labelled diagram to show how you would measure the standard electrode potential of $\text{Cu}^{2+}(\text{aq}) \mid \text{Cu}(\text{s})$ half-cell</p> <p>temperature = 298 K</p> 
16.7	<p>be able to calculate a standard emf, E^\ominus_{cell}, by combining two standard electrode potentials</p>
	<p>Once the E^\ominus of a half-cell is known, the potential difference (or voltage or emf of an electrochemical cell made up of <i>any</i> two half-cells) can be calculated Standard cell potential E^\ominus_{cell} can be calculated by:</p> <ul style="list-style-type: none"> Subtracting the less positive E^\ominus from the more positive E^\ominus value (i.e.) $E^\ominus_{\text{cell}} = \text{more positive } E^\ominus - \text{less positive } E^\ominus$ <p>(By convention, the positive electrode (reduction) is shown on the right and the negative electrode (oxidation) on the left) (i.e.) Subtracting the negative electrode's E^\ominus from positive electrode's E^\ominus (i.e.) $E^\ominus_{\text{cell}} = E^\ominus_{\text{right}} - E^\ominus_{\text{left}}$ (i.e.) $E^\ominus_{\text{cell}} = E^\ominus_{\text{reduction}} - E^\ominus_{\text{oxidation}}$ (oxidation is on the left- reduction on the right)</p> <p>An electrochemical cell is a device for producing an electric current from chemical reactions (which is constructed from two half-cells)</p>

Example: an electrochemical cell consisting of $\text{Zn}^{2+} | \text{Zn}$ and $\text{Cu}^{2+} | \text{Cu}$ half cells



Which can be written as:

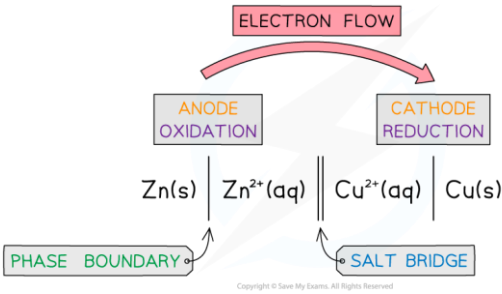


$||$ represents the salt bridge

The emf, $E^{\ominus}_{\text{cell}}$, of the cell is *the difference between the two standard electrode potentials of the two half-cells*

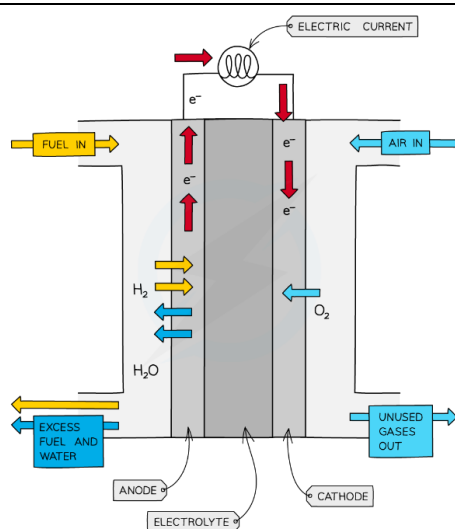
Hence, the emf of the cell is $0.34 - (-0.76) = 1.10\text{V}$ (notice how the emf is positive which indicates that the right-hand electrode, i.e. the copper electrode is the positive electrode of the cell)

You can calculate the emf of the cell from a cell diagram by: $E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{right}} - E^{\ominus}_{\text{left}}$

16.8	be able to write cell diagrams using the conventional representation of half-cells
	<p>Instead of drawing an electrochemical cell system every time, we can draw cell diagrams:</p>  <p>By convention,</p> <ul style="list-style-type: none"> - The half-cell with the greatest negative potential is written on the left (which allows this: $E^\ominus_{\text{cell}} = E^\ominus_{\text{right}} - E^\ominus_{\text{left}}$) - The left cell is being oxidized while the right cell is being reduced - A salt bridge is shown using - State symbols are always included <p>If there is more than one species in solution and the species are on different sides of the half-equation, the different species are separated by a comma (mostly in ion ion with different oxidation numbers)</p> <p>If both species in a half-cell are aqueous, then an inert platinum electrode is used which is recorded on the outside of the cell diagram</p> <p>For eg:</p> <p>Note! The standard hydrogen electrode is always written on the left-hand side</p>
16.9	understand the importance of the conditions when measuring an electrode potential, E
	<p>Electrons flow from the half-cell with the more negative E^\ominus value (negative electrode) to the half-cell with the less negative (i.e. more positive) E^\ominus value (positive electrode)</p> <div style="border: 1px solid black; padding: 5px; margin-top: 10px;"> <p>Note! <i>That is why you should not be confused when you see positive electrode being called a cathode as in this context, electrons are being lost from the negative electrode and electrons are being gained at the positive electrode</i></p> </div>
16.10	be able to use standard electrode potentials to predict the thermodynamic feasibility of a reaction
	<p>E^\ominus values of a species indicate how easily they can get oxidized or reduced (lose or gain electrons)</p> <ul style="list-style-type: none"> - The more positive the value, the easier it is to reduce the species on the left of the half-equation (reaction proceeds in forward direction) - The less positive the value, the easier it is to oxidize the species on the right of the half-equation (reaction proceeds in backward direction) - A reaction is feasible when the E^\ominus_{cell} is positive
16.11	understand that E^\ominus_{cell} is directly proportional to the total entropy change and to $\ln K$ for a reaction
	$T\Delta S^\ominus_{\text{total}} = nFE^\ominus_{\text{cell}}$ <p>where n is the no. of moles of electrons in the cell reaction & F is the faraday constant</p> <ul style="list-style-type: none"> - As n is a constant for a given a cell reaction and F is also a constant, $\Delta S^\ominus_{\text{total}}$ (Total Entropy Change) is proportional to E^\ominus_{cell} (the emf of the cell), at a given temperature - This means if E^\ominus_{cell} is positive, $\Delta S^\ominus_{\text{total}}$ will also be positive (for a reaction as written from left to right in the cell diagram will be thermodynamically feasible) - This also means at a given temperature, $\ln K$ is proportional to E^\ominus_{cell}
16.12	understand the limitations of predictions made using standard electrode potentials, in terms of kinetic stability of systems and departure from standard conditions

	<p>Although we can deduce the thermodynamic feasibility of a reaction using electrode potential, it gives no information on the rate of the reaction</p> <p>In a nutshell,</p> <p>Thermodynamic feasibility can be predicted using standard electrode potentials</p> <p>Do note that even though standard electrode potentials indicate that a reaction is thermodynamically feasible, it may not take place due to:</p> <ul style="list-style-type: none">• Reactants being kinetically stable as the activation energy is very large• Reaction not taking place under standard conditions• Reaction not aqueous <p>A reaction that is not thermodynamically feasible under standard conditions may become feasible when the conditions are altered</p> <ul style="list-style-type: none">- Changing the conditions may alter the electrode potential, E^\ominus, of a half-cell because the position of equilibrium of the half-cell reaction may change <p>Examples of changing the conditions:</p> <ul style="list-style-type: none">- Increasing the concentration of the solutions used in the electrochemical cell makes the cell emf more positive as fewer electrons are produced in the reaction- Increasing the pressure of the cell will make the cell emf more negative as more electrons are produced																																																			
16.13	know that standard electrode potentials are sometimes referred to as standard reduction potentials and can be listed as an electrochemical series																																																			
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very positive are better oxidising agents and will oxidise those species more negative than themselves- Species that are very negative are better reducing agents and will reduce those species less negative than themselves	<i>least powerful oxidising agent</i>	<table><tr><th>OXIDISED FORM</th><th>REDUCED 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$\text{K}^+(\text{aq})$	$\text{K}(\text{s})$																																																			
$\text{Ca}^{2+}(\text{aq})$	$\text{Ca}(\text{s})$																																																			
$\text{Na}^+(\text{aq})$	$\text{Na}(\text{s})$																																																			
$\text{Al}^{3+}(\text{aq})$	$\text{Al}(\text{s})$																																																			
$\text{Zn}^{2+}(\text{aq})$	$\text{Zn}(\text{s})$																																																			
$\text{Cr}^{3+}(\text{aq})$	$\text{Cr}(\text{s})$																																																			
$\text{Fe}^{2+}(\text{aq})$	$\text{Fe}(\text{s})$																																																			
$\text{H}^+(\text{aq})$	$\frac{1}{2}\text{H}_2(\text{g})$																																																			
$\text{Cu}^{2+}(\text{aq})$	$\text{Cu}(\text{s})$																																																			
$\frac{1}{2}\text{I}_2(\text{aq})$	$\text{I}^-(\text{aq})$																																																			
$\text{Ag}^+(\text{aq})$	$\text{Ag}(\text{s})$																																																			
$\frac{1}{2}\text{Br}_2(\text{aq})$	$\text{Br}^-(\text{aq})$																																																			
$\frac{1}{2}\text{Cl}_2(\text{aq})$	$\text{Cl}^-(\text{aq})$																																																			
$\frac{1}{2}\text{F}_2(\text{aq})$	$\text{F}^-(\text{aq})$																																																			
E^\ominus/V																																																				
-3.03																																																				
-2.92																																																				
-2.87																																																				
-2.71																																																				
-1.66																																																				
-0.76																																																				
-0.74																																																				
-0.44																																																				
0.00																																																				
+0.34																																																				
+0.54																																																				
+0.80																																																				
+1.09																																																				
+1.36																																																				
+2.87																																																				
16.14	understand how standard electrode potentials can be used to predict the thermodynamic feasibility of disproportionation reactions																																																			
16.15	be able to carry out both structured and unstructured titration calculations involving redox reactions, including iron(II) ions and potassium manganate(VII) and sodium thiosulfate and iodine																																																			

	<p>Redox Titrations</p> <p>In a titration, the concentration of a solution is determined by titrating with a solution of known concentration</p> <p>In a redox titration, an oxidizing agent is titrated with a reducing agent</p> <p>Electrons are transferred from one species to another</p> <p>Most transition metals change colour when changing oxidation state (so an indicator is not always necessary)</p> <p>You should know these redox titrations below:</p>
	<p>Potassium manganate(VII) Titrations</p> $\text{MnO}_4^- (\text{aq}) + 5\text{e}^- + 8\text{H}^+ (\text{aq}) \rightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l})$ $\text{Fe}^{2+} (\text{aq}) \rightarrow \text{Fe}^{3+} (\text{aq}) + \text{e}^-$ <ul style="list-style-type: none"> In these redox titrations the manganate(VII) is the oxidising agent and is reduced to $\text{Mn}^{2+}(\text{aq})$ The iron is the reducing agent and is oxidised to $\text{Fe}^{3+}(\text{aq})$ and the reaction mixture must be acidified, to excess acid is added to the iron(II) ions before the reaction begins The choice of acid is important, as it must not react with the manganate(VII) ions, so the acid normally used is dilute sulfuric acid <ul style="list-style-type: none"> As it does not oxidise under these conditions and does not react with the manganate(VII) ions
	<p>Iodine-Thiosulfate Titrations</p> $2\text{S}_2\text{O}_3^{2-} (\text{aq}) + \text{I}_2 (\text{aq}) \rightarrow 2\text{I}^- (\text{aq}) + \text{S}_4\text{O}_6^{2-} (\text{aq})$ <ul style="list-style-type: none"> The light brown/yellow colour of the iodine turns paler as it is converted to colourless iodide ions When the solution is a straw colour, starch is added to clarify the end point The solution turns blue/black until all the iodine reacts, at which point the colour disappears This titration can be used to determine the concentration of an oxidizing agent, which oxidizes iodide ions to iodine molecules The amount of iodine is determined from titration against a known quantity of sodium thiosulfate solution
16.16	be able to discuss the uncertainty of measurements and their implications for the validity of the final results
	<p>Percentage uncertainty = (uncertainty / measured value) x 100</p> <ul style="list-style-type: none"> Remember that uncertainty for burette measurements is twice Overall, to reduce the uncertainty in burette readings, you: <ul style="list-style-type: none"> Dilute the chemical in the burette This means that more will be required for the titration Therefore, the overall uncertainty in the burette readings is reduced
16.17	<p>CORE PRACTICALS 13a and 13b</p> <p>Carry out redox titrations with both:</p> <p>i iron(II) ions and potassium manganate(VII)</p> <p>ii sodium thiosulfate and iodine</p>
16.18	<p>understand that fuel cells use the energy released on the reaction of a fuel with oxygen to generate a voltage</p> <p><i>Knowledge that methanol and other hydrogen-rich fuels are used in fuel cells is expected.</i></p>



A **fuel cell** produces a voltage from the chemical reaction of a fuel with oxygen (most commonly, hydrogen is used as the fuel- alternatives include methanol/ethanol and other hydrogen-rich fuels)

A **fuel cell** is an electrochemical cell in which a fuel donates electrons at one electrode and oxygen gains electrons at the other electrode; as the fuel enters the cell, it becomes oxidized which sets up a potential difference (voltage) within the cell

Advantages:

- Alternative to using fossil fuels
- Do not produce carbon dioxide and pollutants
- Lighter and more efficient engines than the ones that use fossil fuels

Disadvantages:

- Hydrogen is explosive when ignited so needs great care when transporting it in terms of compressing the gas/ adsorbing onto the surface of a suitable solid/ absorbing into a suitable material
- Supply of hydrogen mostly comes from methane (non-renewable resource)

16.19

know the electrode reactions that occur in a hydrogen-oxygen fuel cell

Knowledge of hydrogen-oxygen fuel cells with both acidic and alkaline electrolyte is expected.

In the **acidic** hydrogen-oxygen fuel cell:

Both metal electrodes are coated with platinum which catalyses the reactions that take place at the electrodes

At the negative electrode: $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$ $E^\ominus = 0.00\text{V}$

At the positive electrode: $\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}(\text{l})$ $E^\ominus = +1.23\text{V}$

The hydrogen ions (protons) pass through the proton-exchange membrane, which allows them to enter the compartment containing the positive electrode, where they can react with oxygen

The overall cell reaction is: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ $E^\ominus = +1.23\text{V}$

In the **alkaline** hydrogen-oxygen fuel cell:

At the negative electrode: $\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-$ $E^\ominus = -0.83\text{V}$

At the positive electrode: $\frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow 2\text{OH}^-(\text{aq})$ $E^\ominus = +0.40\text{V}$

The overall cell reaction is: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ $E^\ominus = +1.23\text{V}$

!Catalyst is more efficient in alkaline fuel cell

Further suggested practicals:

- investigate the percentage of copper in brass, using iodine-thiosulfate titration
- investigate the percentage of iron in iron tablets, using potassium manganate(VII) titration
- prepare crystals of potassium iodate(VII) and measure their purity